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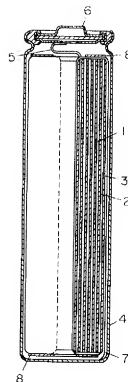
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(54) 【発明の名称】 非水電解液二次電池

(57) 【要約】

【課題】 非水電解液二次電池の過充電時や短絡時の際に、電池温度の急激な上昇を防止して、電解液の漏液を防止する。

【解決手段】 正極および負極と、正負極の間に配されるセパレータと、非水電解液とを用いる非水電解液二次電池において、融解熱の大きいセパレータを用いる。



【特許請求の範囲】

【請求項1】 正、負極とこれらの間に配されるセパレータと非水電解液を備え、前記セパレータは、70～150℃の温度範囲において単位面積あたりの吸熱量が0.07cal/cm²以上であり、厚みが15μm以上30μm以下であるポリオレフィン系微孔性膜からなるセパレータを用いた非水電解液二次電池。

【請求項2】 ポリオレフィン系微孔性膜からなるセパレータが、ポリエチレン単独の微孔性膜もしくはポリエチレン微孔性膜とポリプロピレン微孔性膜を多層化した複合膜である請求項1記載の非水電解液二次電池。

【請求項3】 正極にリチウム含有遷移金属酸化物、負極にリチウムを吸蔵、放出が可能な炭素を用いた請求項1記載の非水電解液二次電池。

【請求項4】 リチウム含有遷移金属酸化物が化学式 Li_xMyO_z (式中MはCo、Ni、Fe、Mnからなる群より選ばれる一種以上の遷移金属；0.5 ≤ x ≤ 1.0、1.0 ≤ y ≤ 2.0) で表される請求項3記載の非水電解液二次電池。

【請求項5】 炭素がX線回折による面間隔d(002)が3.38Å未満であり、またBET法による比表面積が2.0m²/g以上8.0m²/g未満である請求項3記載の非水電解液二次電池。

【請求項6】 非水電解液の溶媒がエチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、プロピオン酸メチル、プロピオン酸エチルからなる群より選ばれる一種以上である請求項1または3記載の非水電解液二次電池。

【請求項7】 非水電解液の溶質が主に6フッ化リン酸リチウムからなる請求項1または3記載の非水電解液二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、非水電解液二次電池の、特にそのセパレータに関するものである。

【0002】

【従来技術】近年、パソコンおよび携帯電話等の電子機器の小型軽量化、コードレス化が急速に進んでおり、これらの駆動用電源として、高エネルギー密度を有する二次電池の開発が要求されている。このような要求に応える電池として、正極に活物質として $LiCoO_2$ や $LiNiO_2$ 、 $LiMn_2O_4$ 等のリチウムに対して4V級の電圧を示すリチウム含有遷移金属酸化物、負極に活物質としてリチウムがインターカレート、デインターカレート可能な炭素材料等が用いられるリチウム二次電池として期待されている。

【0003】リチウム二次電池に用いられるセパレータは、電解液に用いられるエーテルやエステルなどの有機

溶媒に対して難溶性であり、かつ電解液が十分に浸透してリチウムイオンが速やかに移動できる多孔質膜である必要がある。他方で電池の高エネルギー密度化を達成するため、電池活物質をケース内にできるだけ多く詰め込む必要があるが、セパレータの薄肉化が要求される。しかし、電池の極低温充電時には、リチウムイオンの移動が速やかにおこらず負極表面上に樹枝状のリチウムが発生してセパレータを貫通し、内部短絡を引き起こす可能性があるため、セパレータの厚みを厚くしたり、セパレータの孔の径をある程度小さくする必要がある。このため、リチウム二次電池用のセパレータとしては、厚み20～50μmで、空隙率40～70%のポリエチレン樹脂や、ポリプロピレン樹脂、もしくはポリエチレン樹脂とポリプロピレン樹脂の複合膜等が用いられてきた。

【0004】

【発明が解決しようとする課題】リチウム二次電池は、非常に高エネルギーであるため、短絡や過充電等の際、電極活物質と電解液との反応が起こり、その反応熱により電池内の温度が非常に上昇する。この温度上昇にともなう、電解液中の有機溶媒の揮発および電池活物質と電解液との反応によるガス発生が助長され、電池内圧が上昇する。この結果、電池内圧が所定値以上になると、封口板の安全弁が作動してガス放出に伴って電解液も漏出していった。

【0005】本発明はこのような課題を解決するものであり、短絡や過充電時等に電池温度が急激に上昇することを防止して、電池の安全性を向上させるものである。

【0006】

【課題を解決するための手段】この課題を解決するために、本発明はセパレータに70～150℃の温度範囲において、融解熱による単位面積あたりの吸熱量が少なくとも0.07cal/cm²で、厚さ15～30μmのポリオレフィン系微孔性膜を用いるものである。

【0007】これにより、過充電時や短絡時等の電池温度が上昇する際に、正、負極の熱や極板の活物質と電解液との反応による発熱を、セパレータによって効率的に吸熱することができ、電池温度の上昇に伴う電解液中の溶媒の揮発や、活物質と電解液との反応によるガスの急激な発生を抑え、電池内圧の急激な上昇による電解液の電池からの漏れを防止することができる。

【0008】

【発明の実施の形態】本発明は、セパレータに70～150℃の温度領域で0.07cal/cm²以上の吸熱を示し、かつ厚みが15μm以上30μm以下であるポリオレフィン系微孔膜からなるセパレータを用いるものであり、好ましくはポリエチレン膜単独、またはポリエチレン膜とポリプロピレン膜を多層化した複合膜を用いるものである。このような構成をすることにより、電池温度上昇の原因である正、負極の発熱を効果的に吸収し、電池内圧の上昇を抑制することができる。よって、封口板の安全弁が作動せ

ず、電解液の漏液を防止することが可能となる。

【0009】また、正極に $Li_xM_yO_z$ (式中MはCu、Ni、Mnからなる群より選ばれた一種以上の金属； $0.5 \leq x \leq 1.0$ ； $1.0 \leq y \leq 2.0$) で表されるリチウム含有遷移金属酸化物、負極にリチウムの吸蔵、放出が可能でかつ、X線回折による面間隔d(002)が3.38Å未満であり、BET方法による比表面積が $2.0\text{m}^2/\text{g}$ 以上 $8.0\text{m}^2/\text{g}$ 未満の炭素を用い、さらに電解液の溶媒にエチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、プロピオン酸メチル、プロピオン酸エチルからなる群より選ばれた一種以上、溶質に6フッ化リン酸リチウムを用いると、より好ましい。

【0010】

【実施例】以下、本発明の実施例を図面を参照しながら説明する。

【0011】(実施例1)図1に本実施例で用いた非水電解液二次電池の構成断面図を示す。図1に示すように、正極板2と負極板3はセパレータ1によって隔離されており、これらが複数回渦巻状に巻回されてニッケルメッキ鉄製電池ケース4内に収納されている。そして、正極板2からはアルミニウム製正極リード5が引き出されて封口板6に接続され、負極板3からはニッケル製負極リード7が引き出されて電池ケース4の底部に接続されている。8はポリエチレン製絶縁リングで極板群の上底部にそれぞれ設けられている。以下正、負極板等について詳しく説明する。

【0012】正極板は、 $Li_{1.2}CO_3$ と CO_3O_4 とを混合し、900℃で10時間焼成して合成した $LiCO_2$ 100重量部に、導電材としてアセチレンブラック3重量部、結着剤としてフッ素樹脂系結着剤7重量部を混合し、 $LiCO_2$ に対し1%カルボキシメチルセルロース水溶液100重量部に懸濁させて正極合剤ペーストとしており、このペーストを厚さ30μmのアルミ箔の両面に塗工した後、乾燥、圧延ローラーによる圧延を行い、所定の寸法に切断して正極板とした。

【0013】負極板はメソフェーズ小球体を2800℃で黒鉛化し平均粒径が約3μmになるように粉碎、分級したものの(d(002)=3.360Å、BET比表面積=4.0 m^2/g)を用い、これに結着剤として、スチレン/ブタジエンゴム5重量部を混合した後、黒鉛に対し1%カルボキシメチルセルロース水溶液100重量部に懸濁させて負極ペーストとした。このペーストを厚さ20μmの銅箔に負極ペーストを両面に塗工し、乾燥後、圧延ローラーを用いて圧延を行い、所定の寸法に切断して負極板とした。

【0014】そして、正極板にはアルミニウム製、負極

板にはニッケル製のリードをそれぞれ取り付け、DSC(示差熱分析装置)を用いた測定の結果、70~150℃の温度領域で融解熱が0.03cal/cm²で厚みが25μmのポリエチレン微孔性膜からなるセパレータを渦巻状に巻回し、直径17mm、高さ50mmの円筒型電池ケースに収容した。電解液にはエチレンカーボネートとエチルメチルカーボネートを1:3の体積比で混合した溶媒に1.5mol/リットルのLiPF₆を溶解したものをを用い、これを注液した後封口した。これを本発明の電池Aとした。

【0015】(実施例2)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.04cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Bとした。

【0016】(実施例3)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.05cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Cとした。

【0017】(実施例4)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.06cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Dとした。

【0018】(実施例5)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.07cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Eとした。

【0019】(実施例6)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.08cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Fとした。

【0020】(実施例7)DSCを用いた測定の結果、70~150℃の温度領域で融解熱が0.09cal/cm²のセパレータを用いた以外は(実施例1)と同様の電池を作成した。これを本発明の電池Gとした。

【0021】次に、本発明の電池A、B、C、D、E、F、Gを各5セルずつ用意して、環境温度20℃で、上限電圧を4.2Vに設定して、630mAの定電流で2時間充電を行った。

【0022】放電はこの充電状態の電池を放電電流720mA、放電終止電位3.0Vの定電流放電を行った。以上の充電サイクルを20サイクル繰り返した後、満充電状態で加熱を行った。加熱試験は、室温から毎分5℃で150℃まで昇温し、150℃で10分間維持の条件で行った。電池内部の温度および漏液率を(表1)に示す。

【0023】

【表1】

電池	融解熱(cal/cm ²)	電池内温度(℃)	融液率
A	0.03	198	5/5
B	0.04	185	5/5
C	0.05	172	3/5
D	0.06	160	1/5
E	0.07	148	0/5
F	0.08	138	0/5
G	0.09	130	0/5

【0024】(表1)より、融解熱の大きいセパレータを用いると、電池の温度上昇を抑制し、電解液の漏液を防止する効果があった。これは、電池活物質と電解液との反応による発熱をセパレータの融解熱で効果的に吸収し、そのことにより、上記反応に伴うガス発生が抑制されるためである。

【0025】単位面積当り融解熱が同じであるセパレータを用いた場合、セパレータが厚くなるにしたがってセパレータの総吸収熱が大きくなり良い効果が得られるが、厚すぎる場合電池ケースに極板群が入らない等の不都合が生じる。今回実験を行った結果、セパレータの厚みは30 μ m以下が好ましかった。よって、電池のエネルギー密度をある程度確保するためにはセパレータの厚みは30 μ m以下が良い。

【0026】また、セパレータの厚みが10 μ m以下の場合、電池内に含まれるセパレータの量が非常に少なくセパレータに吸収される熱が小さいためガス発生量が多くなった。さらに、セパレータが薄い場合、内部短絡等の危険性が生じるため、安全性を考慮すると15 μ m以上の厚みが好ましい。

【0027】なお、本実験例では、セパレータにポリエチレン微孔性膜を単独で用いた場合について示したが、ポリエチレン微孔性膜とポリプロピレン微孔性膜を多層化したものであっても同様の効果が得られた。

【0028】(実施例8)正極はLiOH \cdot H₂OとN₂(OH)₂とを混合し、750℃で10時間乾燥空気雰囲気下で焼成したLi_{0.5}Ni_{0.5}O₂100重量部に導電材としてアセチレンブラック3重量部、結着剤としてポリフッ化ビニリデン4重量部をN-メチルピロリドン100重量部に混合し懸濁させて正極合剤ペーストとした。この正極合剤ペーストを厚さ30 μ mのアルミ箔に正極合剤ペーストを両面に塗工し、乾燥後、圧延ローラーを用いて圧延を行った。これを所定の寸法の正極板とした。

【0029】負極はメソフェーズ小球体を3000℃で黒鉛

化し平均粒径が約3 μ mになるように粉碎、分級したもの(d(002)=3.355Å、BET比表面積=4.0m²/g)を用いた。ここでd(002)はX線回折により求めた。さらに結着剤として、スチレン/ブタジエンゴム3重量%を混合した後、黒鉛に対し1%カルボキシメチルセルロース水溶液100重量部に懸濁させてペースト状にした。この負極ペーストを厚さ15 μ mの銅箔の両面に塗工し、乾燥後、圧延を行い負極板を製作した。

【0030】そして、正極板にはアルミニウム製、負極板にはニッケル製のリードをそれぞれ取り付け、DSCを用いた測定の結果、70～150℃の温度領域で融解熱が0.07cal/cm²で厚みが25 μ mのポリエチレン製のセパレータを渦巻状に巻回し、直径17mm、高さ50mmの内筒型電池ケースに納入した。電解液にはエチレンカーボネートとエチルメチルカーボネートとを1:3の体積比で混合した溶媒に1.5モル/リットルのLiPF₆を溶解したものをを用い、これを注液した後封口した。これを本発明の電池IIとした。

【0031】(実施例9)負極にメソフェーズ小球体を2800℃で黒鉛化し平均粒径が約3 μ mになるように粉碎、分級したもの(d(002)=3.360Å、BET比表面積=4.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Iとした。

【0032】(実施例10)負極にメソフェーズ小球体を2500℃で黒鉛化し平均粒径が約3 μ mになるように粉碎、分級したもの(d(002)=3.370Å、BET比表面積=4.0m²/g)を用いた以外は(実施例8)と同様の電池を製作した。これを本発明の電池Jとした。

【0033】(実施例11)負極にメソフェーズ小球体を2300℃で黒鉛化し平均粒径が約3 μ mになるように粉碎、分級したもの(d(002)=3.380Å、BET比表面積=4.0m²/g)を用いた以外は(実施例8)と同様の電池を製作した。これを本発明の電池Kとした。

【0034】(実施例12)負極にメソフェーズ小球体

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を2100℃で黒鉛化し平均粒径が約3 μ mになるように粉碎、分級したもの(d(002)=3.390Å、BET比表面積=4.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Iとした。

【0035】以下d(002)が同じでBET比表面積を変えることにより異なる負極を用いて試験を行った。

【0036】(実施例13)負極に平均粒径が約50 μ mの鱗片状黒鉛(d(002)=3.360Å、BET比表面積=0.5m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Mとした。

【0037】(実施例14)負極に平均粒径が約30 μ mの鱗片状黒鉛(d(002)=3.360Å、BET比表面積=2.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Nとした。

【0038】(実施例15)負極に平均粒径が約20 μ mの鱗片状黒鉛(d(002)=3.360Å、BET比表面積=6.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Oとした。

【0039】(実施例16)負極に平均粒径が約10 μ m *

*の鱗片状黒鉛(d(002)=3.360Å、BET比表面積=8.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Pとした。

【0040】(実施例17)負極に平均粒径が約5 μ mの鱗片状黒鉛(d(002)=3.360Å、BET比表面積=10.0m²/g)を用いた以外は(実施例8)と同様の電池を作成した。これを本発明の電池Qとした。

【0041】次に、本発明の電池H、I、J、K、L、M、N、O、P、Qを各5セルずつ用意して、环境温度20℃で、上限電圧を4.2Vに設定して、630mAの定電流で2時間充電を行った。放電はこの充電状態の電池を放電電流720mA、放電終止電位3.0Vの定電流放電を行った。そして、それぞれ20サイクル目の放電容量を初期容量とした。以上の充放電サイクルを繰り返した後、100%充電状態で加熱を行った。加熱試験は、室温から毎分5℃で150℃まで昇温し、150℃で10分間維持の条件で行った。電池内部の温度および漏液率を(表2)に示す。

【0042】

【表2】

電池	d(002)(Å)	比表面積(m ² /g)	初期容量(mAh/g)	電池内温度(℃)	漏液率
H	3.335	4.0	830	156	0/5
I	3.360	4.0	800	151	0/5
J	3.370	4.0	770	147	0/5
K	3.380	4.0	680	142	0/5
L	3.390	4.0	590	138	0/5
M	3.360	0.5	830	140	0/5
N	3.360	2.0	900	146	0/5
O	3.360	6.0	930	157	0/5
P	3.360	8.0	885	159	2/5
Q	3.360	10.0	938	187	5/5

【0043】(表2)より、漏液率の点で黒鉛層間の面間隔は電池HからLの範囲で差はなかった。しかし、電池の初期容量の点からみると、d(002)が3.38Å以上になると初期容量は著しく低下している。これは、黒鉛の層間距離が大きくなりすぎるとインターカレートし得るリチウム量が減少するためである。また、d(002)が小さい程電池内温度が上昇しているが、これは黒鉛化度が高い程電解液との反応性が高くなり発熱量が大きくなるからである。よって、d(002)は3.350Å以上3.380Å未満が好ましい。

【0044】さらに(表2)の電池MからQより、BET比表面積が大きくなる程電解液との反応面積が増大し、発熱量が大きくなり電池内温度が上昇する。ここで、BET比表面積が8m²/g以上になると電池内温度の上昇が大きく、電解液との反応に伴うガス発生も増大し漏液が起こり始める。よって、BET比表面積は8m²/g未満でなければならない。そこで、BET比表面積が9m²/g未満であれば漏液率の点からは良いと考えられる。しかし上記同様電池の初期容量の点からみると、BET比表面積が0.5m²/gの初期容量が著しく低下してい

る。これは、反応面積の減少によるレート特性の低下が原因である。よって、BET比表面積は小さければよいわけではなく、 $2.0\text{m}^2/\text{g}$ 以上でなければならない。

【0045】以上のように、X線回折による面間隔 $d(002)$ が 3.35\AA 以上 3.38\AA 未満であり、またBET法による比表面積が $2.0\text{m}^2/\text{g}$ 以上 $8.0\text{m}^2/\text{g}$ 未満である炭素の場合、電池の初期容量を低下させることなく、電池の温度上昇時にも電池活物質と電解液との反応によるガス発生が少なく、電池内圧の上昇を抑制することができる。よって、封口板の安全弁が作動せず、電解液の漏液を防止することができる。

【0046】なお、本実験例では、負極炭素に球状黒鉛であるメソフェーズ小球体を用いた場合について示したが、塊状黒鉛についても本発明の範囲で同様の効果が得られた。

【0047】(実施例18) 正極は $\text{Li}_2\text{C}_2\text{O}_3$ と MnO とを混合し、 800°C で30時間乾燥空気雰囲気下で焼成した $\text{Li}_2\text{Mn}_2\text{O}_4$ 100重量部に導電材としてアセチレンブラック3重量部、結着剤としてフッ素樹脂系結着剤7重量部を混合し、 $\text{Li}_2\text{Mn}_2\text{O}_4$ に対し1%カルボキシメチルセルロース水溶液100重量部に懸濁させて正極合剤ペーストとした。この正極合剤ペーストを厚さ $30\mu\text{m}$ のアルミ箔に正極合剤ペーストを両面に塗工し、乾燥後、圧延ローラーを用いて圧延を行った。これを所定の寸法の正極板とした。

【0048】負極はメソフェーズ小球体を 2800°C で黒鉛化し平均粒径が約 $3\mu\text{m}$ になるように粉砕、分級したものを $d(002)=3.360\text{\AA}$ 、BET比表面積 $=4.0\text{m}^2/\text{g}$ を用いた。さらに結着剤として、スチレン/ブタジエンゴム5重量部を混合した後、黒鉛に対し1%カルボキシメチルセルロース水溶液100重量部に懸濁させてペースト状にした。厚さ $20\mu\text{m}$ の銅箔に負極ペーストを両面に塗工し、乾燥後、圧延ローラーを用いて圧延を行った。これを所定の寸法の負極板とした。

【0049】そして、正極板にはアルミニウム製、負極板にはニッケル製のリードをそれぞれ取り付け、DSCを用いた測定の結果、 $70\sim 150^\circ\text{C}$ の温度領域で融解熱が $0.07\text{cal}/\text{cm}^2$ で厚みが $25\mu\text{m}$ のポリエチレン製のセパレータを渦巻状に巻回し、直径 17mm 、高さ 50mm の円筒型電池ケースに納入した。電解液にはエチレンカーボネートとエチルメチルカーボネートとを1:3の体積比で混合した溶媒に1.5モル/リットルの LiPF_6 を溶解したものを、これを注液した後封口した。これを本発明の電池Rとした。

【0050】(実施例19) エチレンカーボネートとジエチルカーボネートとを1:3の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Sとした。

【0051】(実施例20) エチレンカーボネートとジメチルカーボネートとを1:3の体積比で混合した

溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Tとした。

【0052】(実施例21) エチレンカーボネートとエチルメチルカーボネートとプロピレンカーボネートとを1:2:1の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Uとした。

【0053】(実施例22) エチレンカーボネートとジエチルカーボネートとプロピオン酸メチルとを1:2:1の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Vとした。

【0054】(実施例23) エチレンカーボネートとジエチルカーボネートとプロピオン酸エチルとを1:2:1の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Wとした。

【0055】(実施例24) エチレンカーボネートと1,2-ジメチルキシエタンとを1:3の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Xとした。

【0056】(実施例25) エチレンカーボネートとテトラヒドロフランとを1:3の体積比で混合した溶媒を用いた以外は(実施例18)と同様の電池を作成した。これを本発明の電池Yとした。

【0057】次に、本発明の電池R、S、T、U、V、W、X、Yを各5セルずつ用意して、環境温度 20°C で、上限電圧を 4.2V に設定して、 630mA の定電流で2時間充電を行った。放電はこの充電状態の電池を放電電流 720mA 、放電終止電位 3.0V の定電流放電を行った。以上の充電サイクルを20サイクル繰り返した後、100%充電状態で加熱を行った。加熱試験は、室温から毎分 5°C で 150°C まで昇温し、 150°C で10分間維持の条件で行った。電池内部の温度および漏液率を(表3)に示す。

【0058】

【表3】

電池	溶媒組成	電池内温度(℃)	漏液率
R	EC:DWC=1:3	144	0/5
S	EC:DEC=1:3	150	0/5
T	EC:DWC=1:3	139	0/5
U	EC:DEC:PC=1:2:1	140	0/5
V	EC:DEC:MP=1:2:1	146	0/5
W	EC:DEC:BP=1:2:1	144	0/5
X	EC:DMS=1:3	150	3/5
Y	EC:THF=1:3	164	5/5

【0059】電解液の溶媒としてエチレンカーボネートは熱的安定性に優れているが、融点が34℃と高く、また粘性が高いため含有率を大きくするとリチウムイオンの導電性が低下する。このため、この実験においてはエチレンカーボネートの含有率を25%で一定にして行った。

【0060】(表3)より、電解液の溶媒としてテトラヒドロフランなどの環状エーテルを用いた場合、エチレンカーボネート、エチルメチルカーボネートなどの環状および鎖状カーボネートを用いた場合と比べて電池内温度の上昇が大きかった。これは、電解液の溶媒として環状エーテルを用いた場合、環状および鎖状カーボネートと比べて電池活物質と電解液の溶媒との反応による発熱が大きく、その温度上昇によりガス発生が起こりやすくなるためである。また、電解液の溶媒として1,2-ジメチキシエタンなどの鎖状エーテルを用いた場合、環状エーテルと比べて電池内温度の上昇は抑制された。しかし、このような温度でも環状および鎖状カーボネートを用いた場合と比べて電池活物質と電解液の溶媒との反応によるガス発生量が多いため電池内圧が上昇し、電解液の漏液が起こった。さらに、環状および鎖状エーテルは酸化

電位がエステル系と比べて低く、このため充電時に電解液の分解反応が起こり、電池容量が小さい。このような理由から電解液の溶媒に環状および鎖状エーテルを用いることは電池性能を低下させるため不適切である。

【0061】以上のように、電解液の溶媒として、エチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、プロピオン酸メチル、プロピオン酸エチルからなる群より選ばれる一種以上であることが好ましい。

【0062】また、本実施例では、正極にLiCoO₂、LiNiO₂、LiMn₂O₄を用いたが、Feを用いても良く、Mg、Co、Ni、Fe、Mnからなる群より選ばれる一種以上の遷移金属で0.5≤x≤1.0、1.0≤y≤2.0であるLi_xM_yO₂であれば同様の効果が得られた。

【0063】

【発明の効果】以上のように本発明では、セパレータに70～150℃の温度範囲において、融解熱による単位面積あたりの吸熱量が少なくとも0.07cal/cm²で、厚さ15～30μmのポリオレフィン系微孔性膜を用いているので、電池温度上昇時の発熱をセパレータで効率的に吸収することができ、電池内圧の急激な上昇やこれに起因する漏液を防止することができる。

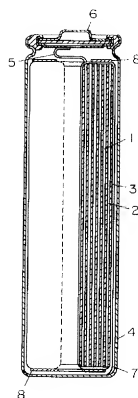
【図面の簡単な説明】

【図1】本発明の実施例における非水電解液二次電池の構成図

【符号の説明】

- 1 セパレータ
- 2 正極板
- 3 負極板
- 4 電池ケース
- 5 正極リード
- 6 封口板
- 7 負極リード
- 8 絶縁リング

【図1】



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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the rise of battery internal pressure due to the sudden rise of battery temperature at the time of a short circuit or overcharge, or the leakage of an electrolyte due to the rise of the battery internal

pressure, by constituting the separator of a specific microporous film, in this secondary battery equipped with positive and negative electrodes, the separator arranged between these electrodes, and a nonaqueous electrolyte.

SOLUTION: A separator 1 is constituted of a polyolefine fine porous film which is a microporous film wherein heat absorbing quantity to a unit area at 70-150°C is 0.07cal/cm² or more, a thickness of 15-30μm, preferably PE alone, or a composite film where a PE microporous coat and a PP microporous film and a PP microporous coat are made multilayer. In this secondary battery, it is preferable to use an Li containing transition metal oxide to a positive electrode 2, carbon capable of storing and emitting Li to a positive electrode 3, one or more selected from ethylene, propylene, dimethyl, diethyl, and ethyl-methyl-carbonate, etc., to the solvent of a nonaqueous electrolyte, and lithium phosphate hexafluoride to the solvent of the nonaqueous electrolyte.

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CLAIMS

[Claim(s)]

[Claim 1] For said separator, thickness is a nonaqueous electrolyte rechargeable battery using the separator with which the amount of endoergic per unit area is

two or more 0.07 cal/cm, and it consists [in / have the separator and nonaqueous electrolyte which are allotted between forward, a negative electrode, and these, and / a 70-150-degree C temperature requirement] of 15-micrometer or more a polyolefin micropore membrane it is [polyolefin micropore membrane] 30 micrometers or less.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 whose separator which consists of a polyolefin micropore membrane is the bipolar membrane which multilayered polyethylene independent a micropore membrane or a polyethylene micropore membrane, and a polypropylene micropore membrane.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 which used lithium content transition-metals oxide for the positive electrode, and used for the negative electrode occlusion and the carbon which can be emitted for the lithium.

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 3 by which a lithium content transition-metals multiple oxide is expressed with a chemical formula Li_xMyO_2 (transition metals more than a kind chosen from the group which the inside M of a formula becomes from Co, nickel, Fe, and Mn; $0.5 \leq x \leq 1.0$, $1.0 \leq y \leq 2.0$).

[Claim 5] The nonaqueous electrolyte rechargeable battery according to claim 3

whose spacing $d(002)$ according [carbon] to an X diffraction is less than 3.38Å and whose specific surface area by the BET adsorption method is under 8.0m²/g more than 2.0m²/g.

[Claim 6] The nonaqueous electrolyte rechargeable battery according to claim 1 or 3 which is more than a kind as which the solvent of nonaqueous electrolyte is chosen from the group which it becomes from ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methyl propionate, and ethyl propionate.

[Claim 7] The nonaqueous electrolyte rechargeable battery according to claim 1 or 3 with which the solute of nonaqueous electrolyte mainly consists of a 6 phosphorus-fluoride acid lithium.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is the thing especially about the separator of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] In recent years, the formation of small lightweight of electronic equipment, such as a personal computer and a cellular phone, and cordless-ization are progressing quickly, and development of the rechargeable battery which has a high energy consistency is demanded as these power sources for a drive. The lithium secondary battery with which the carbon material which can be intercalated and a lithium can deintercalate as an active material is used for the lithium content transition-metals oxide in which a 4V class electrical potential difference is shown [as opposed to / as an active material / the lithium of LiCoO_2 , LiNiO_2 , and LiMn_2O_4 grade], and a negative electrode is expected [as opposed to / as a cell which meets such a demand / the positive electrode] as a cell which especially has a high voltage and a high energy consistency.

[0003] The separator used for a lithium secondary battery needs to be the porous membrane which is poorly soluble, and the electrolytic solution fully permeates and a lithium ion can move promptly to organic solvents used for the electrolytic solution, such as the ether and ester. In order to attain high energy consistency-ization of a cell on the other hand, it is necessary to stuff as many cell active materials in a case as possible, and the thinning of a separator is required. However, migration of a lithium ion does not start promptly, but since the lithium of arborescence may be generated, a separator may be penetrated and an internal short circuit may be caused on a negative-electrode front face, it

is necessary to thicken thickness of a separator or to make the path of the hole of a separator to some extent small at the time of very-low-temperature charge of a cell. For this reason, as a separator for lithium secondary batteries, it is 20-50 micrometers in thickness, and the bipolar membrane of polyethylene resin of 40 - 70% of void contents, polypropylene resin or polyethylene resin, and polypropylene resin etc. has been used.

[0004]

[Problem(s) to be Solved by the Invention] Since a lithium secondary battery is very high energy, in the cases, such as a short circuit and overcharge, the reaction of an electrode active material and the electrolytic solution occurs, and the temperature in a cell rises very much with the heat of reaction. In connection with this temperature rise, the generation of gas by volatilization of the organic solvent in the electrolytic solution and the reaction of a cell active material and the electrolytic solution is promoted, and cell internal pressure rises. Consequently, when cell internal pressure became beyond the predetermined value, the relief valve of an obturation plate operated and the electrolytic solution was also leaked in connection with the gas evolution.

[0005] This invention solves such a technical problem, prevents that cell temperature rises rapidly at the time of a short circuit or overcharge etc., and raises the safety of a cell.

[0006]

[Means for Solving the Problem] In order to solve this technical problem, in a 70-150-degree C temperature requirement, the amount of endoergic per unit area by the heat of fusion is 0.07 cal/cm² at least, and this invention uses a polyolefin micropore membrane with a thickness of 15-30 micrometers for a separator.

[0007] By this, in case the cell temperature at the time of overcharge and a short circuit etc. rises, forward and generation of heat by the reaction of the heat of a negative electrode, the active material of a plate, and the electrolytic solution Endoergic can be efficiently carried out with a separator, rapid generating of the gas by volatilization of the solvent in the electrolytic solution accompanying the rise of cell temperature and the reaction of an active material and the electrolytic solution can be suppressed, and the liquid spill from the cell of the electrolytic solution by the rapid rise of cell internal pressure can be prevented.

[0008]

[Embodiment of the Invention] The bipolar membrane which multilayered polyethylene film independence or the polyethylene film, and the polypropylene film preferably is used for this invention using the separator with which endoergic [two or more 0.07 cal/cm] is shown in a separator in a 70-150-degree C temperature field, and thickness consists of a 15-micrometer or more polyolefine

system micropore film which is 30 micrometers or less. By carrying out such a configuration, forward [which caused the cell temperature rise], and generation of heat of a negative electrode can be absorbed effectively, and the rise of cell internal pressure can be controlled. Therefore, the relief valve of an obturation plate does not operate but it becomes possible to prevent a liquid spill of the electrolytic solution.

[0009] Moreover, the lithium content transition-metals oxide expressed with Li_xMyO_2 (the metal more than a kind chosen from the group which the inside M of a formula becomes from Co, nickel, and Mn; $0.5 \leq x \leq 1.0$; $1.0 \leq y \leq 2.0$) by the positive electrode, The occlusion of a lithium and emission are possible to a negative electrode, and the spacing d by the X diffraction (002) is less than 3.38Å. The specific surface area by the BET approach uses the carbon of under 8.0m²/g more than 2.0m²/g. Furthermore, to the solvent of the electrolytic solution, ethylene carbonate, propylene carbonate, It is more desirable when 6 phosphorus-fluoride acid lithium is used for a solute more than a kind chosen from the group which consists of dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methyl propionate, and ethyl propionate.

[0010]

[Example] Hereafter, the example of this invention is explained, referring to a drawing.

[0011] (Example 1) The configuration sectional view of the nonaqueous electrolyte rechargeable battery used for drawing 1 by this example is shown. As shown in drawing 1, it is isolated with the separator 1, and these are wound in the shape of a multiple-times swirl, and the positive-electrode plate 2 and the negative-electrode plate 3 are contained in the nickel-plating iron cell case 4. And from the positive-electrode plate 2, the positive-electrode lead 5 made from aluminum is pulled out, and it connects with the obturation plate 6, and from the negative-electrode plate 3, the negative-electrode lead 7 made from nickel is pulled out, and it connects with the pars basilaris ossis occipitalis of the cell case 4. 8 is prepared in the raised bottom section of a group of electrode with the insulating ring made from polyethylene, respectively. The forward one, a negative-electrode plate, etc. are explained in detail below.

[0012] In the LiCoO₂ 100 weight section which the positive-electrode plate mixed Li₂CO₃ and Co₃O₄, and calcinated for 10 hours and was compounded at 900 degrees C Mix the acetylene black 3 weight section as electric conduction material, and the fluororesin system binder 7 weight section is mixed as a binder. it suspends in the carboxymethyl-cellulose water-solution 100 weight section 1% to LiCoO₂ -- making -- a positive electrode -- a mixture -- after considering as the paste and carrying out coating of this paste to both sides of aluminum foil with a thickness of 30 micrometers, desiccation and rolling with a rolling roller were

performed, and it cut in the predetermined dimension, and considered as the positive-electrode plate.

[0013] After the negative-electrode plate mixed styrene / butadiene rubber 5 weight section as a binder to this using what was ground and classified so that a mesophase microsphere might be graphitized at 2800 degrees C and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.360\text{\AA}$, BET specific surface area= $4.0\text{m}^2/\text{g}$), the carboxymethyl-cellulose water-solution 100 weight section was made to suspend it 1% to a graphite, and it was considered as the negative-electrode paste. This paste was carried out to copper foil with a thickness of 20 micrometers, and coating of the negative-electrode paste was carried out to both sides, and it rolled out after desiccation using the rolling roller, it cut in the predetermined dimension, and considered as the negative-electrode plate.

[0014] And the lead made from nickel was attached in the product made from aluminum, and the negative-electrode plate at the positive-electrode plate, respectively, and the separator with which the heat of fusion consists of a polyethylene micropore membrane whose thickness is 25 micrometers by 0.03 cal/cm^2 in a 70-150-degree C temperature field was spirally held in the cylindrical cell case with winding, a diameter [of 17mm], and a height of 50mm as a result of the measurement using DSC (differential thermal analyzer). It

obtured, after pouring this in the electrolytic solution using what dissolved 1.5 mols [l.] LiPF₆ in the solvent which mixed ethylene carbonate and ethyl methyl carbonate by the volume ratio of 1:3. This was made into the cell A of this invention.

[0015] (Example 2) As a result of the measurement using DSC, except that the heat of fusion used the separator of 0.04 cal/cm² in the 70-150-degree C temperature field, the same cell as (an example 1) was created. This was made into the cell B of this invention.

[0016] (Example 3) As a result of the measurement using DSC, except that the heat of fusion used the separator of 0.05 cal/cm² in the 70-150-degree C temperature field, the same cell as (an example 1) was created. This was made into the cell C of this invention.

[0017] (Example 4) As a result of the measurement using DSC, except that the heat of fusion used the separator of 0.06 cal/cm² in the 70-150-degree C temperature field, the same cell as (an example 1) was created. This was made into the cell D of this invention.

[0018] (Example 5) As a result of the measurement using DSC, except that the heat of fusion used the separator of 0.07 cal/cm² in the 70-150-degree C temperature field, the same cell as (an example 1) was created. This was made into the cell E of this invention.

[0019] (Example 6) Using DSC, except that the heat of fusion used the separator of 0.08 cal/cm² in the 70-150-degree C temperature field as a result of ***** , the same cell as (an example 1) was created. This was made into the cell F of this invention.

[0020] (Example 7) As a result of the measurement using DSC, except that the heat of fusion used the separator of 0.09 cal/cm² in the 70-150-degree C temperature field, the same cell as (an example 1) was created. This was made into the cell G of this invention.

[0021] Next, five every cels each of cells A, B, C, D, E, F, and G of this invention were prepared, the upper limit electrical potential difference was set as 4.2V with the environmental temperature of 20 degrees C, and charge was performed by 630mA constant current for 2 hours.

[0022] Discharge performed 720mA of discharge currents, and constant-current discharge of discharge termination potential 3.0V for the cell of this charge condition. The above charge-and-discharge cycle was heated in the state of the full charge after 20 cycle ***** . The temperature up of the heat test was carried out from the room temperature to 150 degrees C at 5 degrees C/m, and it was performed on condition that maintenance for 10 minutes at 150 degrees C. The temperature and the rate of a liquid spill inside a cell are shown in (Table 1).

[0023]

[Table 1]

電池	融解熱(cal/cm ²)	電池内温度 (°C)	漏液率
A	0.03	198	5/5
B	0.04	185	5/5
C	0.05	172	3/5
D	0.06	160	1/5
E	0.07	148	0/5
F	0.08	138	0/5
G	0.09	130	0/5

[0024] From (Table 1), when the large separator of the heat of fusion was used, the temperature rise of a cell was controlled and it was effective in preventing a liquid spill of the electrolytic solution. This is because generation of heat by the reaction of a cell active material and the electrolytic solution is effectively absorbed with the heat of fusion of a separator and the generation of gas accompanying the above-mentioned reaction is controlled by that.

[0025] When the separator with the same heat of fusion is used per unit area, the total heat of absorption of a separator becomes large, good effectiveness is acquired as a separator becomes thick, but when too thick, un-arranging [of a group of electrode not going into a cell case] arises. As a result of experimenting this time, the thickness of a separator had desirable 30 micrometers or less. Therefore, in order to secure the energy density of a cell to some extent, the

thickness of a separator has good 30 micrometers or less.

[0026] Moreover, when the thickness of a separator was 10 micrometers or less, since the heat with which the amount of the separator contained in a cell is absorbed by the separator very few was small, the amount of generation of gas increased. Furthermore, since danger, such as an internal short circuit, arises when a separator is thin, when safety is taken into consideration, the thickness of 15 micrometers or more is desirable.

[0027] In addition, although this example of an experiment showed the case where a polyethylene micropore membrane was independently used for a separator, the same effectiveness was acquired even if it multilayered the polyethylene micropore membrane and the polypropylene micropore membrane.

[0028] (Example 8) a positive electrode -- $\text{LiOH} \cdot \text{H}_2\text{O}$ and nickel $(\text{OH})_2$ are mixed, it mixes as electric conduction material in the LiNiO_2 100 weight section calcinated under the 10-hour dry air ambient atmosphere at 750 degrees C, the polyvinylidene fluoride 4 weight section is mixed in the N-methyl pyrrolidone 100 weight section as the acetylene black 3 weight section and a binder, and it suspends -- making -- a positive electrode -- a mixture -- it considered as the paste. this positive electrode -- a mixture -- a paste -- aluminum foil with a thickness of 30 micrometers -- a positive electrode -- a mixture -- coating of the paste was carried out to both sides, and it rolled out after desiccation using the

rolling roller. This was made into the positive-electrode plate of a predetermined dimension.

[0029] The negative electrode used what was ground and classified so that a mesophase microsphere might be graphitized at 3000 degrees C and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.355\text{\AA}$, BET specific surface area = $4.0\text{m}^2/\text{g}$). It asked for $d(002)$ according to the X diffraction here. Furthermore, as a binder, after mixing styrene / 3 % of the weight of butadiene rubber, the carboxymethyl-cellulose water-solution 100 weight section was made to suspend 1% to a graphite, and it was made the shape of a paste. Coating of this negative-electrode paste was carried out to both sides of copper foil with a thickness of 15 micrometers, after desiccation, rolling was performed and the negative-electrode plate was produced.

[0030] And the lead made from nickel was attached in the product made from aluminum, and the negative-electrode plate at the positive-electrode plate, respectively, and the heat of fusion supplied the separator made from polyethylene whose thickness is 25 micrometers spirally to the cylindrical cell case with winding, a diameter [of 17mm], and a height of 50mm by $0.07\text{ cal}/\text{cm}^2$ in the 70-150-degree C temperature field as a result of the measurement using DSC. It obturated, after pouring this in the electrolytic solution using what dissolved 1.5 mols [l.] LiPF₆ in the solvent which mixed

ethylene carbonate and ethyl methyl carbonate by the volume ratio of 1:3. This was made into the cell H of this invention.

[0031] (Example 9) The same cell as (an example 8) was created except having used what was ground and classified so that a mesophase microsphere might be graphitized at 2800 degrees C to a negative electrode and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.360\text{\AA}$, BET specific surface area= $4.0\text{m}^2/\text{g}$). This was made into the cell I of this invention.

[0032] (Example 10) The same cell as (an example 8) was created except having used what was ground and classified so that a mesophase microsphere might be graphitized at 2500 degrees C to a negative electrode and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.370\text{\AA}$, BET specific surface area= $4.0\text{m}^2/\text{g}$). This was made into the cell J of this invention.

[0033] (Example 11) The same cell as (an example 8) was created except having used what was ground and classified so that a mesophase microsphere might be graphitized at 2300 degrees C to a negative electrode and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.380\text{\AA}$, BET specific surface area= $4.0\text{m}^2/\text{g}$). This was made into the cell K of this invention.

[0034] (Example 12) The same cell as (an example 8) was created except having used what was ground and classified so that a mesophase microsphere might be graphitized at 2100 degrees C to a negative electrode and mean

particle diameter might be set to about 3 micrometers ($d(002) = 3.390\text{\AA}$, BET specific surface area= $4.0\text{m}^2/\text{g}$). This was made into the cell L of this invention.

[0035] Following d (002) was the same and it examined using a different negative electrode by changing a BET specific surface area.

[0036] (Example 13) The same cell as (an example 8) was created except having used for the negative electrode the scale-like graphite ($d(002) = 3.360\text{\AA}$, BET specific surface area= $0.5\text{m}^2/\text{g}$) whose mean particle diameter is about 50 micrometers. This was made into the cell M of this invention.

[0037] (Example 14) The same cell as (an example 8) was created except having used for the negative electrode the scale-like graphite ($d(002) = 3.360\text{\AA}$, BET specific surface area= $2.0\text{m}^2/\text{g}$) whose mean particle diameter is about 30 micrometers. This was made into the cell N of this invention.

[0038] (Example 15) The same cell as (an example 8) was created except having used for the negative electrode the scale-like graphite ($d(002) = 3.360\text{\AA}$, BET specific surface area= $6.0\text{m}^2/\text{g}$) whose mean particle diameter is about 20 micrometers. This was made into the cell O of this invention.

[0039] (Example 16) The same cell as (an example 8) was created except having used for the negative electrode the scale-like graphite ($d(002) = 3.360\text{\AA}$, BET specific surface area= $8.0\text{m}^2/\text{g}$) whose mean particle diameter is about 10 micrometers. This was made into the cell P of this invention.

[0040] (Example 17) The same cell as (an example 8) was created except having used for the negative electrode the scale-like graphite ($d(002) = 3.360\text{\AA}$, BET specific surface area= $10.0\text{m}^2/\text{g}$) whose mean particle diameter is about 5 micrometers. This was made into the cell Q of this invention.

[0041] Next, five every cels each of cells H, I, J, K, L, M, N, O, P, and Q of this invention were prepared, the upper limit electrical potential difference was set as 4.2V with the environmental temperature of 20 degrees C, and charge was performed by 630mA constant current for 2 hours. Discharge performed 720mA of discharge currents, and constant-current discharge of discharge termination potential 3.0V for the cell of this charge condition. And discharge capacity of 20 cycle eye was made into initial capacity, respectively. After repeating the above charge-and-discharge cycle, it heated in the state of charge 100%. The temperature up of the heat test was carried out from the room temperature to 150 degrees C at 5 degrees C/m, and it was performed on condition that maintenance for 10 minutes at 150 degrees C. The temperature and the rate of a liquid spill inside a cell are shown in (Table 2).

[0042]

[Table 2]

電池	d(002)(Å)	比表面積(m^2/g)	初期容量(mAh/g)	電池内温度($^{\circ}\text{C}$)	漏液率
H	3.335	4.0	830	156	0/5
I	3.360	4.0	800	151	0/5
J	3.370	4.0	770	147	0/5
K	3.380	4.0	690	142	0/5
L	3.393	4.0	590	138	0/5
M	3.360	0.5	830	140	0/5
N	3.360	2.0	900	146	0/5
O	3.350	6.0	930	157	0/5
P	3.360	8.0	935	159	2/5
Q	3.360	10.0	938	187	5/5

[0043] From (Table 2), there was no spacing between graphite layers in respect of the rate of a liquid spill, and there was no difference in the range of L from Cell H. However, in terms of the initial capacity of a cell, if d (002) becomes 3.38Å or more, initial capacity will fall remarkably. This is for the amount of lithiums which can be intercalated if the distance between layers of a graphite becomes large too much to decrease. Moreover, although whenever [cell internal temperature] is going up so that d (002) is small, this is because reactivity with the electrolytic solution becomes high and calorific value becomes large so that a degree of graphitization is high. Therefore, 3.350Å or more less than 3.380Å of d (002) is desirable.

[0044] From the cell [further / (Table 2)] M, from Q, reaction area with the electrolytic solution increases, so that a BET specific surface area becomes large, calorific value becomes large, and whenever [cell internal temperature] goes up. Here, if a BET specific surface area becomes more than $8\text{m}^2/\text{g}$, the rise of whenever [cell internal temperature] will be large, the generation of gas accompanying a reaction with the electrolytic solution will also increase, and a liquid spill will begin to take place. Therefore, a BET specific surface area must be under $8\text{m}^2/\text{g}$. Then, if a BET specific surface area is under $8\text{m}^2/\text{g}$, it will be thought that it is good from the point of the rate of a liquid spill. However, like the above, in terms of the initial capacity of a cell, when a BET specific surface area is $0.5\text{m}^2/\text{g}$, initial capacity is falling remarkably. The fall of the rate property according [this] to reduction of reaction area is the cause. Therefore, a BET specific surface area should not necessarily be just small, and if it is ***** above $2.0\text{m}^2/\text{g}$, there is. [no]

[0045] As mentioned above, without reducing the initial capacity of a cell, when it is carbon whose spacing d by the X diffraction (002) is 3.35\AA or more less than 3.38\AA and whose specific surface area by the BET adsorption method is under $8.0\text{m}^2/\text{g}$ more than $2.0\text{m}^2/\text{g}$, there is little generation of gas by the reaction of a cell active material and the electrolytic solution also at the time of the temperature rise of a cell, and it can control the rise of cell internal pressure at it.

Therefore, the relief valve of an obturation plate cannot operate but a liquid spill of the electrolytic solution can be prevented.

[0046] In addition, although this example of an experiment showed the case where the MEZOFESU microsphere which is nodular graphite was used to negative-electrode carbon, effectiveness with the same said of a massive graphite in the range of this invention was acquired.

[0047] (Example 18) a positive electrode -- Li_2CO_3 and MnO_2 are mixed, in the LiMn_2O_4 100 weight section calcinated under the 30-hour dry air ambient atmosphere at 800 degrees C, the acetylene black 3 weight section is mixed as electric conduction material, the fluororesin system binder 7 weight section is mixed as a binder, and it suspends in the carboxymethyl-cellulose water-solution 100 weight section 1% to LiMn_2O_4 -- making -- a positive electrode -- a mixture -- it considered as the paste. this positive electrode -- a mixture -- a paste -- aluminum foil with a thickness of 30 micrometers -- a positive electrode -- a mixture -- coating of the paste was carried out to both sides, and it rolled out after desiccation using the rolling roller. This was made into the positive-electrode plate of a predetermined dimension.

[0048] The negative electrode used what was ground and classified so that a mesophase microsphere might be graphitized at 2800 degrees C and mean particle diameter might be set to about 3 micrometers ($d(002) = 3.360\text{\AA}$, BET

specific surface area=4.0m²/g). Furthermore, as a binder, after mixing styrene / butadiene rubber 5 weight section, the carboxymethyl-cellulose water-solution 100 weight section was made to suspend 1% to a graphite, and it was made the shape of a paste. Coating of the negative-electrode paste was carried out to copper foil with a thickness of 20 micrometers to both sides, and it rolled out after desiccation using the rolling roller. This was made into the negative-electrode plate of a predetermined dimension.

[0049] And the lead made from nickel was attached in the product made from aluminum, and the negative-electrode plate at the positive-electrode plate, respectively, and the heat of fusion supplied the separator made from polyethylene whose thickness is 25 micrometers spirally to the cylindrical cell case with winding, a diameter [of 17mm], and a height of 50mm by 0.07 cal/cm² in the 70-150-degree C temperature field as a result of the measurement using DSC. It obtained, after pouring this in the electrolytic solution using what dissolved 1.5 mols [/l.] LiPF₆ in the solvent which mixed ethylene carbonate and ethyl methyl carbonate by the volume ratio of 1:3. This was made into the cell R of this invention.

[0050] (Example 19) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate and diethyl carbonate by the volume ratio of 1:3. This was made into the cell S of this invention.

[0051] (Example 20) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate and dimethyl carbonate by the volume ratio of 1:3. This was made into the cell T of this invention.

[0052] (Example 21) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate, ethyl methyl carbonate, and propylene carbonate by the volume ratio of 1:2:1. This was made into the cell U of this invention.

[0053] (Example 22) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate, diethyl carbonate, and methyl propionate by the volume ratio of 1:2:1. This was made into the cell V of this invention.

[0054] (Example 23) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate, diethyl carbonate, and ethyl propionate by the volume ratio of 1:2:1. This was made into the cell W of this invention.

[0055] (Example 24) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate and 1 and 2-dimethoxyethane by the volume ratio of 1:3. This was made into the cell X of this invention.

[0056] (Example 25) The same cell as (an example 18) was created except having used the solvent which mixed ethylene carbonate and a tetrahydrofuran by the volume ratio of 1:3. This was made into the cell Y of this invention.

[0057] Next, five every cels each of cells R, S, T, U, V, W, X, and Y of this invention were prepared, the upper limit electrical potential difference was set as 4.2V with the environmental temperature of 20 degrees C, and charge was performed by 630mA constant current for 2 hours. Discharge performed 720mA of discharge currents, and constant-current discharge of discharge termination potential 3.0V for the cell of this charge condition. The above charge-and-discharge cycle was heated in the state of charge 100% after 20 cycle *****. The temperature up of the heat test was carried out from the room temperature to 150 degrees C at 5 degrees C/m, and it was performed on condition that maintenance for 10 minutes at 150 degrees C. The temperature and the rate of a liquid spill inside a cell are shown in (Table 3).

[0058]

[Table 3]

電池	溶媒組成	電池内温度 (°C)	漏液率
R	EC:DMC=1:3	1 4 4	0 / 5
S	EC:DEC=1:3	1 5 0	0 / 5
T	EC:DMC=1:3	1 3 9	0 / 5
U	EC:DEC:PC=1:2:1	1 4 0	0 / 5
V	EC:DEC:MP=1:2:1	1 4 6	0 / 5
W	EC:DEC:EP=1:2:1	1 4 4	0 / 5
X	EC:DMS=1:3	1 5 0	3 / 5
Y	EC:THF=1:3	1 6 4	5 / 5

[0059] Although ethylene carbonate is excellent in thermal stability as a solvent of the electrolytic solution, since viscosity is high, if the melting point makes content greatly as high as 34 degrees C, the conductivity of a lithium ion will fall. For this reason, in this experiment, at 25%, content of ethylene carbonate was fixed and was performed.

[0060] When cyclic ether, such as a tetrahydrofuran, was used as a solvent of the electrolytic solution, compared with the case where annular [, such as ethylene carbonate and ethyl methyl carbonate] and chain-like carbonate are used, the rise of whenever [cell internal temperature] was larger than (Table 3). This is for generation of heat by the reaction of a cell active material and the solvent of the electrolytic solution to be large compared with annular and chain-like carbonate, and for the generation of gas to become easy to happen by

the temperature rise, when cyclic ether is used as a solvent of the electrolytic solution. Moreover, when the chain-like ether, such as 1 and 2-dimethoxyethane, was used as a solvent of the electrolytic solution, the rise of whenever [cell internal temperature] was controlled compared with cyclic ether. However, since there were many amounts of generation of gas by the reaction of a cell active material and the solvent of the electrolytic solution compared with the case where annular and chain-like carbonate are used also at such temperature, cell internal pressure rose, and the liquid spill of the electrolytic solution took place. Furthermore, oxidation potential is low compared with an ester system, for this reason, the decomposition reaction of the electrolytic solution occurs at the time of charge, and annular and the chain-like ether have a small cell capacity. Since it is such, it is unsuitable to use annular and the chain-like ether for the solvent of the electrolytic solution in order to reduce the cell engine performance.

[0061] As mentioned above, it is desirable that it is more than a kind chosen from the group which consists of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methyl propionate, and ethyl propionate as a solvent of the electrolytic solution.

[0062] Moreover, in this example, although LiCoO_2 , LiNiO_2 , and LiMn_2O_4 were used for the positive electrode, Fe could be used, and when it was Li_xMyO_2 which are $0.5 \leq x \leq 1.0$ and $1.0 \leq y \leq 2.0$ in the transition metals more than a

kind chosen from the group which M becomes from Co, nickel, Fe, and Mn, the same effectiveness was acquired.

[0063]

[Effect of the Invention] As mentioned above, by this invention, since the amount of endoergic per unit area by the heat of fusion uses the polyolefin micropore membrane with a thickness of 15-30 micrometers for the separator by 0.07 cal/cm² at least in the 70-150-degree C temperature requirement, generation of heat at the time of a cell temperature rise can be efficiently absorbed with a separator, and the liquid spill resulting from a rapid rise and this rapid of cell internal pressure can be prevented.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The block diagram of the nonaqueous electrolyte rechargeable battery in the example of this invention

[Description of Notations]

1 Separator

2 Positive-Electrode Plate

3 Negative-Electrode Plate

4 Cell Case

5 Positive-Electrode Lead

6 Obturation Plate

7 Negative-Electrode Lead

8 Insulating Ring